The Molybdenum Isotope Paleoredox Proxy: Prospects and Progress

A. D. ANBAR[1], G. A. WILLIAMS[2] AND T. W. LYONS[3]

[1]Dept. of Geological Sciences and Dept. of Chemistry & Biochemistry, Arizona State University, Tempe, AZ, USA (anbar@asu.edu)
[2]Dept. of Geological Sciences, Arizona State University, Tempe, AZ, USA (Gwyneth.Williams@asu.edu)
[3]Dept. of Earth Sciences, U. C. Riverside, Riverside, CA, USA (timothy.lyons@ucr.edu)

The oxygenation of the oceans has varied through time but the timing and extent of these variations are not well understood, nor do we understand the connections between changes in atmospheric and ocean oxygenation. The development and refinement of ocean paleoredox proxies is therefore a high priority.

The molybdenum (Mo) stable isotope system is emerging as a valuable tool for investigating ocean paleoredox (Anbar, 2004). To first order, Mo enters the oceans via rivers and is removed in oxic environments by adsorption to Mn oxides and in sulfidic settings via scavenging of Mo oxythiomolybdates. The isotopic contrast between these sinks is ~ 2 ‰ due to fractionation during adsorption to Mn-oxides (Barling and Anbar, 2004). Hence, the steady-state Mo isotope composition of the oceans should reflect the balance between Mo removal to Mn-oxides vs. removal in sulfidic ("euxinic") settings. This system is particularly valuable because it may constrain regional or global ocean redox, rather than only local redox, as a result of the long ocean residence time of this element.

Mo isotope systematics are already being applied to ancient ocean redox puzzles (e.g., Arnold et al, 2004). Quantitative application requires better understanding of a number of parameters, especially the importance of suboxic (O_2 < 5 mM) settings for Mo removal and isotope fractionation. Studies in such settings reveal Mo isotopes fractionation.

We have investigated this phenomenon in ancient black shales. Prior work on the Devonian Oatka and Geneseo Fms. of western New York indicates that while the Oatka Fm. was deposited under sulfidic bottom waters, the Geneseo Fm. was deposited under less intensely reducing conditions. We find that Oatka Fm. $\delta^{97/95}$Mo values are 0.95-1.30, with most values >1.1. In comparison, Geneseo Fm. values are systemtically lighter, 0.68-0.93. The systematic offset is similar to that seen between euxinic and suboxic sediments today, and $\delta^{97/95}$Mo and DOP values covary. The data indicate that Mo isotopes were fractionated during uptake into Oatka and Geneseo sediments with DOP < 0.6. These data lead to three conclusions: (a) covariation of $\delta^{97/95}$Mo and DOP cautions against use of sediments from suboxic settings as recorders of contemporaneous seawater; (b) conversely, if mean ocean $\delta^{97/95}$Mo for a particular time is independently known, $\delta^{97/95}$Mo-DOP relationships may constrain local depositional redox conditions; (c) with respect to the Mo ocean budget, because fractionation during uptake to suboxic sediments is similar in direction and magnitude to fractionation during adsorption on Mn oxides the effects of expansion of suboxic seafloor on the Mo isotope system could partially offset the effects of contraction of oxic seafloor. Hence, the Mo isotope system may underestimate the extent of ancient seafloor redox change.

A. D. Anbar (2004). Molybdenum stable isotopes: Observations, interpretations and directions. *Rev. Mineral. Geochem.* **55**: 429-454.

G. L. Arnold, A. D. Anbar, J. Barling and T. W. Lyons (2004). Molybdenum isotope evidence of widespread anoxia in mid-Proterozoic oceans. *Science* **304**: 87-90.

J. Barling and A. D. Anbar (2004). Molybdenum isotope fractionation during adsorption by manganese oxides. *Earth Planet. Sci. Lett.* **217**: 315-329.